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(54) Title: FLUORO-CHEMICAL OIL AND WATER REPELLENTS

(57) Abstract: A polymer having at least one urea linkage derived by contacting (1) at least one polyisocyanate, or mixture of polyisocyanates, (2) at least one fluorocarbon alcohol, fluorocarbon thiol or fluorocarbon amine, (3) at least one straight or branched chain alcohol, amine or thiol, and then (4) at least one linking agent is disclosed which provides oil repellency and water repellency to substrates without curing at high temperature after application, and imparts laundry air dry performance to the substrates.

WO 01/10922 A1

## **TITLE OF INVENTION**

Fluorochemical Oil and Water Repellents

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## **FIELD OF THE INVENTION**

This invention relates to fluorochemical compositions that provide oil repellency and water repellency properties to substrates. This invention further relates to a method for imparting oil- and water-repellent properties to various substrates and the resulting treated substrates.

## **BACKGROUND OF THE INVENTION**

Conventional oil and water repellent coating compositions for fibers or fibrous substrates, such as the fluoro(meth)acrylate copolymers, require a relatively high temperature cure (e.g., at 165°C) after application to develop the desired surface properties. Such temperatures are associated with certain disadvantages, such as reduced dye retention, high energy use, or discoloration. Furthermore, on laundering, the oil and water repellency imparted to the substrates using prior art compositions are not durable after laundering without a subsequent heat treatment step. The substrates do not fully regain their desired surface effects when air-dried at ambient temperatures. While tumble drying at elevated temperatures or heat or steam pressing can usually at least partially restore the surface properties, such post laundering heat treatments are undesirable for outerwear fabrics and delicate fabrics, for instance those best laundered in cool water, such as silks and woolsens.

Audenaert, et al., in WO 97/44375, discloses compositions that impart oil and water repellency to fabrics. The compositions incorporate a chain transfer agent into an oligomer by reacting the agent with ethylenically-unsaturated fluorinated monomers. The functionalized oligomer is subsequently reacted with a polyfunctional isocyanate.

It is desirable to provide durable oil repellency and water repellency to substrates that do not need a high temperature cure after application of the composition. It is also desirable that the repellency properties are durable and the substrates recover their properties after laundering without a heating step. The present invention provides compositions that impart these properties.

### SUMMARY OF THE INVENTION

The present invention comprises a polymer having at least one urea linkage derived by contacting (1) at least one polyisocyanate, or mixture of polyisocyanates, (2) at least one fluorocarbon alcohol, fluorocarbon thiol or fluorocarbon amine, (3) at least one alcohol, amine or thiol, and then (4) at least one linking agent.

The present invention further comprises a polymer having at least one urea linkage derived by contacting (1) at least one polyisocyanate, or mixture of polyisocyanates, (2) at least one fluorocarbon alcohol, fluorocarbon thiol or fluorocarbon amine, (3) at least one alcohol, amine or thiol, (4) at least one chemical species containing at least one group capable of reacting with an isocyanate and at least one quaternizable group, and then (5) at least one linking agent.

The present invention further comprises a method of imparting oil repellency and water repellency to a fibrous substrate or a wood, masonry or natural leather substrate comprising contacting said substrate with a polymer as described above. No high temperature curing step is required after application of the polymer.

The present invention further comprises a method for imparting oil repellency and water repellency to a synthetic suede leather substrate comprising contacting said substrate with

A) a polymer having at least one urea linkage derived by reacting (1) at least one polyisocyanate, or mixture of polyisocyanates, (2) at least one fluorocarbon alcohol, fluorocarbon thiol, or fluorocarbon amine, (3) at least one

alcohol, amine or thiol, and then (4) optionally at least one linking agent, wherein the polymer has a particle size of a minimum of about 250 nm, or

5 B) a polymer prepared by contacting (1) at least one polyisocyanate, or mixture of polyisocyanates, (2) at least one fluorocarbon alcohol, fluorocarbon thiol or fluorocarbon amine, (3) at least one alcohol, amine or thiol, and then (4) at least one chemical species containing at least one group capable of reacting with an isocyanate and at least one quaternizable group, and then (5) optionally at least one linking agent, wherein the polymer has a particle size of a minimum of 250 nm.

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The present invention further comprises a fibrous substrate, or a wood, masonry, or natural leather substrate, or a synthetic suede leather substrate having oil repellency and water repellency treated with the appropriate polymer as described above. The fibrous substrates maintain the repellency properties through laundering and air drying without a heating step or treatment (laundry air dry) when the alcohol, amine or thiol used to prepare the polymer is branched chain, or is a mixture of branched and straight chain. The synthetic suede leather substrates maintain the repellency properties through laundering and air drying without a heating step or treatment when the alcohol, amine or thiol used to prepare the polymer is a mixture of branched and straight chain. The presence of branched chain alcohol, amine or thiol in preparation of the polymer is beneficial to hand feel in the treated synthetic suede leather.

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### DETAILED DESCRIPTION OF THE INVENTION

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Tradenames and trademarks are indicated herein by capitalization. The urethane-based oil and water repellent polymers of the present invention comprise branched polymers having at least one urea linkage per molecule and are derived by contacting (1) at least one polyisocyanate, or a mixture of polyisocyanates, which predominately contains at least three isocyanate groups per molecule (Reactant 1), (2) at least one fluorocarbon alcohol, fluorocarbon thiol, or fluorocarbon amine (Reactant 2), (3) at least one branched or straight chain alcohol, branched or straight chain amine, or branched or straight chain thiol (Reactant 3), and (4) sufficient linking agent to react with all remaining

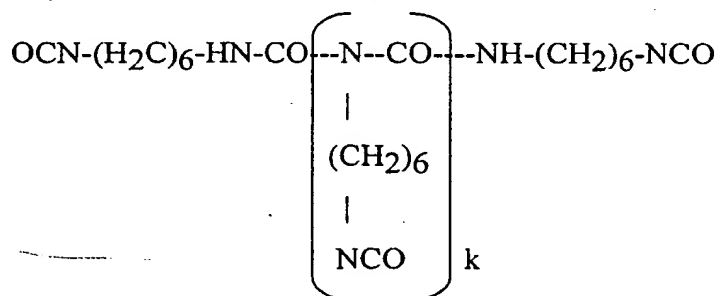
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isocyanate groups (Reactant 4). These are hereinafter identified as Reactants 1 - 4. By the term "polyisocyanates" is meant tri- and higher isocyanates and the term includes oligomers. The molar amounts of Reactants 2 and 3 are selected to be insufficient to react with all the isocyanate groups. The remaining isocyanate groups are consumed by Reactant 4.

The most practical method to prepare the polymers of this invention when the linking agent (Reactant 4) is water is first to contact Reactants 1 - 3, and then react the product with an excess of Reactant 4, thereby avoiding the need for precise measurement of relatively small amounts of water.

The polyisocyanate reactant (Reactant 1) provides the branched polymer backbone of the polymer. Any polyisocyanate having predominately three or more isocyanate groups, or any isocyanate precursor of a polyisocyanate having predominately three or more isocyanate groups, is suitable for use in this invention. It is recognized that minor amounts of diisocyanates may remain in such products. An example of this is a biuret containing residual small amounts of hexamethylene diisocyanate. Particularly preferred as Reactant 1 are hexamethylene diisocyanate homopolymers having the structure of Formula 1.

Formula 1:

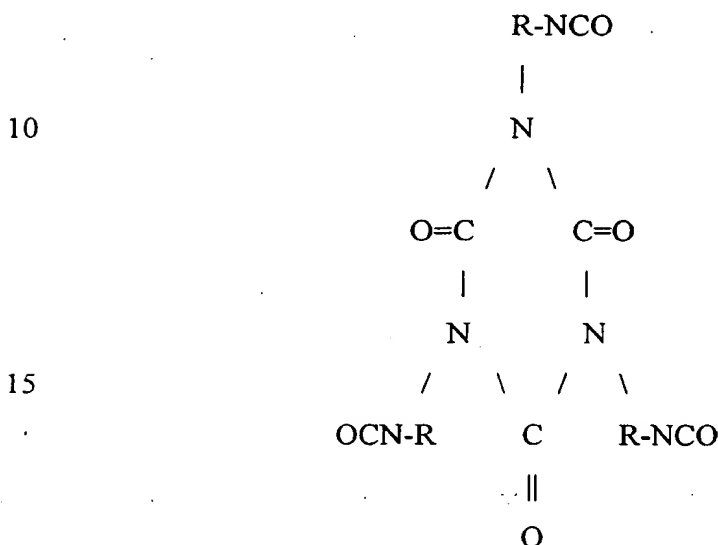


wherein k averages about 1.8. These are commercially available, for instance as DESMODUR N-100 from Bayer Corporation, Pittsburgh PA. DESMODUR N-100 is a hexamethylene diisocyanate-based polymeric isocyanate containing biuret groups. While individual homopolymers having  $k = 1, 2$ , etc., are suitable for preparing the polyurethane polymers of the present invention, this specific

homopolymer is only available in admixture with substantial amounts (50% or more) of homopolymers having  $k$  greater than 1, i.e., substantial amounts of tetra- and higher polyisocyanates.

Also suitable for use as Reactant 1 are hydrocarbon diisocyanate-derived isocyanurate trimers that can be represented by Formula 2.

Formula 2:



wherein R is a divalent hydrocarbon group, preferably aliphatic, alicyclic, aromatic, or arylaliphatic. For example, R is hexamethylene, toluene, or cyclohexylene, and is preferably hexamethylene, which is available as DESMODUR N-3300 (a hexamethylene diisocyanate-based isocyanurate). Other triisocyanates useful for the purposes of this invention are those obtained by reacting three moles of toluene diisocyanate with 1,1,1-tris-(hydroxymethyl)ethane or 1,1,1-tris-(hydroxymethyl)propane. The isocyanurate trimers of toluene diisocyanate and 3-isocyanatomethyl-3,4,4-trimethylcyclohexyl isocyanate are other examples of triisocyanates useful for the purposes of this invention, as is methine-tris-(phenylisocyanate). Precursors of polyisocyanates, such as diisocyanates, are also suitable for use in the present invention as substitutes for the polyisocyanates.

The fluorocarbon alcohol, fluorocarbon thiol, or fluorocarbon amine (Reactant 2) provides the oil- and soil-repellency and contributes to the water



repellency of the polymer. The fluorocarbon alcohol, fluorocarbon thiol, or fluorocarbon amine reactant suitable for use in the present invention has the structure:



wherein  $R_f$  is a  $C_4 - C_{20}$  linear or branched fluorocarbon chain,  $X$  is a divalent linking radical of formula  $-(CH_2)_n$  or  $-SO_2N(R_1)-CH_2CH_2-$ , wherein  $n$  is 1 to about 20; and  $R_1$  is an alkyl of 1 to about 4 carbon atoms; and

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$Y$  is  $-O-$ ,  $-S-$ , or  $-N(R_2)-$ , where  $R_2$  is  $H$  or  $R_1$ .

More particularly  $R_f$  is  $C_qF_{(2q+1)}$  wherein  $q$  is from about 4 to about 20, or mixtures thereof. Preferred examples of  $R_f-X-$  include 1) mixtures of

- 15  $F(CF_2)_q(CH_2)_n-$  wherein  $q$  and  $n$  are as previously defined, and 2)  $F(CF_2)_qSO_2N(R_1)CH_2CH_2-$  wherein  $q$  and  $R_1$  are as previously defined. An example of mixture 1) includes the group of formula  $F(CF_2CF_2)_nCH_2CH_2OH$ , wherein  $n$  has values selected from 2, 3, 4, 5, 6, 7, 8, 9, and 10, said fluorochemical compounds being present in the proportions shown as
- 20 compositions (i) or (ii) in Table 1:

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Table 1. Compositions of Fluoroalcohols of Formula  $F(CF_2CF_2)_nCH_2CH_2OH$ .

n	Composition by weight %	
	(i)	(ii)
2	0 - 3	
3	27 - 37	0 - 3
4	28 - 32	45 - 52
5	14 - 20	26 - 32
6	8 - 13	10 - 14
7	3 - 6	2 - 5
8	0 - 2	0 - 2
9	0 - 1	0 - 1
10	0 - 1	0 - 1

The alcohol, amine, or thiol reactants (Reactant 3) contribute to the water repellency properties of the polymer. Suitable for use herein as the alcohol, amine, or thiol reactant are straight chain or branched alcohols, straight chain or branched amines, or straight chain or branched thiols. Primary alcohols are preferred since such alcohols are more readily reacted with the isocyanate groups than secondary or tertiary alcohols for steric reasons. While Reactant 3 can be either straight chain or branched chain to obtain the repellency properties using a low temperature cure, a mixture of branched and straight chain moieties is typically used. For Class A Substrates, utilizing all branched or a proportion of branched chain alcohols, amines, or thiols is important to provide the laundry air dry characteristics of the substrates of this invention, probably by adding to the chain disorder. While a broad molar ratio of branched chain alcohol, amine, or thiol to straight chain alcohol, amine, or thiol is operable, the molar ratio of branched chain to straight chain is preferably in the range 1:0 to 1:1 and most preferably is 1:0 to 1:0.33.

For Class C substrates, utilizing a mixture of branched and straight chain alcohols provides the laundry air dry characteristic to substrates to which the polymers of this invention have been applied. Having branched chain alcohols

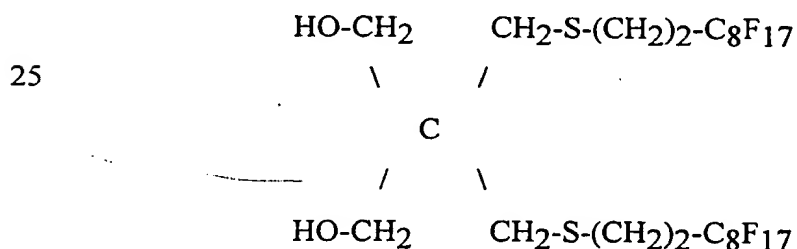
present is important for good hand feel in the treated substrates.

Suitable straight chain alcohols, amines, or thiols include those of the structure  $H(CH_2)_x-OH$ ,  $H(CH_2)_x-NH_2$ , or  $H(CH_2)_x-SH$ , respectively wherein  $x$  is 12 to 20, or mixtures thereof. Preferred is Reactant 3 wherein  $x$  is 16 to 18 such as the readily available stearyl alcohol (1-octadecanol).

Suitable branched chain alcohols, amines, or thiols include those of the structure  $C_yH_{(2y+1)}-CH_2-OH$ ,  $C_yH_{(2y+1)}-CH_2-NH_2$ , or  $C_yH_{(2y+1)}-CH_2-SH$  wherein  $y$  is in the range 15 to 19, or mixtures thereof. An example is ISOFOL 18T, a mixture of branched chain alcohols comprising 2-hexyl- and 2-octyl-decanol, and 2-hexyl- and 2-octyl-dodecanol, available from CONDEA-Vista Co., Houston TX.

The linking agent (Reactant 4) is a compound capable of reacting with isocyanate groups remaining after contacting Reactants 1 to 3, thereby linking two isocyanate-terminated molecules together and increasing the molecular weight of the product. Typically a compound containing a hydroxy group is used. While water is the most commonly used linking agent, other difunctional compounds such as glycols are also suitable for use herein. When a linking agent other than water is selected, a stoichiometric insufficiency is used, as discussed below. A fluorinated diol is also suitable, such as the structure of Formula 3.

Formula 3:



Such a fluorinated diol, clearly, acts as both a linking agent (Reactant 4) and as a fluorocarbon alcohol (Reactant 2). An example of such a diol is LODYNE 941, available from Ciba Specialty Chemicals, High Point, NC.

A second embodiment of the present invention comprises a polymer having at least one urea linkage derived by contacting Reactants 1 to 3 as described above with an additional reactant comprising a chemical species with at least one group capable of reacting with an isocyanate and at least one quaternizable group. This additional reactant is either a new Reactant A or is Reactant 3 or Reactant 4. Reactant A is of formula X-R-Y wherein X is a quaternizable amine or ammonia type of functional group; Y is OH, NH<sub>2</sub> or SH; and R is an aromatic, aliphatic, polyalkyl or polyether group or R is the nitrogen atom in a quaternizable amine. In addition, X-R-Y may be multifunctional. This additional reactant is added in an amount equivalent to up to 15%, and preferably 3 - 9%, of the total available isocyanate groups in Reactant 1. Representative compositions are shown in Tables 2 and 3. Reactant A is contacted with Reactants 1 to 3 prior to the final use of a linking agent to complete reaction of the isocyanate groups. If the additional reactant is Reactant 3, an example of such a chemical species is N,N-dimethylethanolamine. If the additional reactant is Reactant 4, an example of such a chemical species is the diol N-methyl diethanolamine. In this embodiment, the polymerized quaternizable Reactant A may be protonated or alkylated to provide a pendant cationic group. Such pendant groups can aid in the preparation of the polymer dispersion or provide a self-dispersing branched polymer, reducing or eliminating the need for the separate addition of surfactants or dispersants. This means that an emulsification step is not always necessary in the present invention. The self-dispersing polymers thus obtained provide dispersions stable over wider pH ranges than polymers dispersed with added dispersants

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The polymers of the present invention are prepared in a suitable dry solvent that is free of groups that react with isocyanate groups. Organic solvents are employed. Ketones are the preferred solvents, methylisobutyl ketone (MIBK) is particularly preferred for convenience and availability. The reaction of the alcohols with the polyisocyanate is optionally carried out in the presence of a catalyst, such as dibutyltin dilaurate or tetraisopropyltitanate, typically in an amount of about 0.1 - 1.0%.

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The ratio of reactants on a molar basis per 100 isocyanate groups is shown in Table 2 below:

Table 2. Reactant Ratios (as mole % based on total available isocyanate groups in Reactant 1)

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Reactant Ratios for Class A and B Substrates			Preferably	
Reactant Number and Name	from	to	from	To
Fluoro-alcohol, -thiol, or -amine (Reactant 2)	31	51	36	46
Alcohol, amine, or thiol (Reactant 3)	31	51	36	46
Optional N-substituted hydroxyamine (Reactant A)	0	15	3	9
Total reactants less linking agent	70	97	75	85
Thus for Class A and B Substrates, the linking agent is 3 to 30, preferably 15 to 25. The ratio of straight to branched alcohols, amines, or thiols is as previously specified above in the description of Reactant 3.				
Reactant Ratios for Class C Substrates			Preferably	
Reactant Number and Name	from	to	from	to
Fluoro-alcohol, -thiol, or -amine (Reactant 2)	31	60	45	59
Alcohol, amine, or thiol (Reactant 3)	20	40	20	30
Optional N-substituted hydroxyamine (Reactant A)	0	40	20	35
Total reactants less linking agent	80	100	90	98
Thus for Class C Substrates, the linking agent is 0 to 20, preferably 2 to 10.				

Since the equivalent weights of Reactants 1 - 4 vary according to the specific reactants chosen, the amounts are necessarily calculated in molar ratios. Examples of specific polymer compositions showing weight ratios are shown in

10 Table 3 below.

Table 3. Calculated Polymer Compositions by Weight to  
Demonstrate Two Compositions of Table 2.

Reactant No. and Name	Wt. (g)	Moles	Wt. %	Mole %
<b>Polymer "a":</b>				
1. Isocyanate	376.8	1.9854	40.1	54.9
2. Fluoroalcohol	287.4	0.6155	30.5	17.0
3. Alcohols*	276.6	1.0126	29.4	28.1
Non-isocyanate reactants as mole % of isocyanate groups				82.1
<b>Polymer "b":</b>				
1. Isocyanate	376.8	1.9854	36.1	50.8
2. Fluoroalcohol	472.9	1.0126	45.3	25.9
3. Alcohols*	168.2	0.6155	16.1	15.7
3. Dimethylethanol-amine	26.5	0.2978	2.5	7.6
Non-isocyanate reactants as mole % of isocyanate groups				96.9

\* linear and branched.

Under rigorously quantitative control, it is possible to prepare the polymers of the present invention by mixing all the reactants. However, a more practical method to prepare the polymers of this invention when Reactant 4 is water is first to contact Reactants 1 - 3, and then react the product with an excess of water, thereby avoiding the need for precise measurement of relatively small amounts of water. Similarly, when Reactant 4 is a linking agent other than water, again a stoichiometric insufficiency of Reactant 4 is used, such that a small proportion of the isocyanate groups, e.g., 1 - 2 molar %, remain unreacted. This ensures that no unreacted linking agent remains in the final product. After the linking agent has reacted, a small excess of water is added, ensuring no unreacted isocyanates remain in the final product.

The Reactants 1 - 3 are charged in the desired proportions under dry conditions (for example under dry nitrogen) and typically heated to a temperature

of at least about 90°C to complete the reaction. The completeness of the reaction is measured by quenching an aliquot in water, and using gas chromatography to demonstrate the absence of unreacted alcohols, amines, or thiols in the drowned sample. The sum of the reactants is typically insufficient to react completely the available isocyanate groups, thus providing a driving force to complete reactions with all the alcohol, amine, or thiol reactants. Typically about 15 - 25 molar % of the isocyanate groups remain unreacted prior to the addition of the linking agent. When this initial reaction with Reactants 1 - 3 is completed, the linking agent is added. When the linking agent is water, an excess is added to react with all remaining isocyanate groups and simultaneously to increase the molecular weight.

Suitable substrates for the application of the polymers of this invention are divided into three classes, based on the preferred loading of the polymer onto the substrate. Hereinafter, these are described as "Class A Substrates" or fibrous substrates; "Class B Substrates" or wood, natural leather, and masonry substrates; and "Class C Substrates", or synthetic suede leather. Preferred substrates are those of Classes A and C. Class A substrates include substrates such as fibers, yarns, fabrics, carpeting, and other articles made from filaments, fibers, or yarns derived from natural, modified natural, or synthetic polymeric materials. Specific representative examples of Class A Substrates are cotton, silk, regenerated cellulose, nylon, wool, fiber-forming linear polyesters, fiber-forming polyacrylonitrile, cellulose nitrate, cellulose acetate, ethyl cellulose, and paper. Class B Substrates include natural leather, wood, pressed or otherwise hardened wood composites, and masonry such as stone unglazed porcelain and tile, grout, porous concrete and the like. Suitable substrates for this invention also include blends of fibrous Class A Substrates with other Class B substrates. Class C Substrates, synthetic suede leathers, generally comprise two layers, a base resin-treated fibrous substrate and a top layer containing resin and optional additives such as pigments. The top layer is buffed or abraded to make the suede surface. The resins are poly(vinyl chloride) or, more preferably, polyurethane. Such polyurethane leathers are described by Sugawara in Koka Patent No. Sho 54(19179)-18991 and by Civardi and Hutter in the Kirk-Othmer Encyclopedia of Chemical Technology, Vol. 14, pp.231 - 249 (John Wiley & Sons, Inc., New York NY, 1981, ISBN 0-47102067-2) under "Leatherlike Material".

For use with Class A and B Substrates the reaction mass, containing solvent but now no remaining isocyanate groups, is emulsified in a blender, homogenizer, or ultrasonic mixer with the addition of an emulsifying agent or surfactant. The solvent is stripped from the emulsion by vacuum distillation to provide a typically turbid polymer dispersion, and the dispersion concentration typically adjusted with water to about 20 - 40% solids by weight, for convenience in handling. The solids adjustment is made to provide a product dispersion having a fluorine concentration of from about 5 to about 15% by weight. Adjustment of the dispersion concentration is not critical. Lower fluorine concentrations in the dispersion will require the use of larger amounts of the dispersion in treating the substrates to produce the desired fluorine level in the dry substrate as described below. Conversely higher fluorine concentrations in the dispersion would require less dispersion in the substrate treatment.

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Emulsification as described above is also suitable for class C substrates, provided that the particle size is adjusted to be a minimum of 250 nm.

The emulsifying aids used are conventional cationic, anionic, nonionic and amphoteric surfactants and compatible mixtures of such emulsifying aids.

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Choosing the emulsifying aid or aids is well known by those skilled in the art.

The selection is necessarily made for compatibility with other surfactants in the system. For instance, anionic surfactants, including carboxylates, sulfonates, sulfates, and phosphates, are used frequently for the natural leather industry,

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while cationic surfactants, including quaternary ammonium salts and amines are used frequently in the textile industry. Preferred cationic surfactants are amine salts (used alone or as mixtures with nonionics) such as H-N-(R<sub>3</sub>)(R<sub>4</sub>)(R<sub>5</sub>), where in R<sub>3</sub> is a long chain alkyl group of 10-24 carbons and R<sub>4</sub> and R<sub>5</sub> are short chain alkyl groups with 1 to 8 carbon atoms or hydrogen. The counteranion can be a halogen ion, HSO<sub>4</sub><sup>-</sup>, or CH<sub>3</sub>COO<sup>-</sup>. The amount of surfactant is chosen to impart sufficient laundry air dry oil and water repellency, and the amount is increased or decreased as desired.

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Examples of such emulsifying aids are as follows. Examples of anionic aids include WITCONATE 30DS, available from Witco Corp., Greenwich, CT; SULFONATE AA10, available from Tennessee Chemical, Atlanta, GA; and DOWFAX 2A1, available from Dow Chemical Co., Midland, MI. Examples of cationic aids are ARMEEN DM-18 and ARQUAD 2HT-75 available from Akzo Nobel, Chicago, IL. Examples of nonionic aids include MERPOL HCS, available from Stepan Co., Northfield, IL; and IGEPAL CO630, available from Rhodia, Cranberry, NJ. An example of an amphoteric aid is MAFO 13, available from PPG/Mazer, Gurnee, IL.

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The present invention further comprises a method of imparting oil repellency and water repellency to various substrates comprising contacting said substrate with the above described polymer. Oil repellency correlates with repelling oil-based soils. Similarly, water repellency correlates with repelling water-based soils or stains. Thus the method of the present invention is useful to impart repellency of oil and water based soils and stains to substrate surfaces.

As previously noted suitable substrates for the application of the polymers of this invention are divided into three classes, described as "Class A Substrates" or fibrous substrates; "Class B Substrates" or wood, natural leather, and masonry substrates; and "Class C Substrates", or synthetic suede leather.

The polymers of the present invention are useful for treating Class A Substrates wherein (i) the oil and water repellent properties of the coated substrate develop when the conventional high temperature cure is replaced with a low temperature cure, and (ii) the oil and water repellency is recovered after laundering without the need for a heat treatment. By the term "high temperature cure" is meant conventional curing at about 165°C. By the term "low temperature cure" is meant a curing at between ambient temperature and about 160°C. By the term "laundry air dry" is meant the ability of a repellent coating to recover or retain its surface properties after laundering or cleaning by drying at ambient temperatures and without the application of heat during drying or pressing at elevated temperatures.

It should be understood that curing temperatures above the low temperature cure range will also cause the oil- and water-repellency to develop. Similarly, the use of elevated temperatures for drying or pressing will also allow oil- and water-repellency to recover. However, the options of the low temperature cure and laundry air dry provide a number of advantages. Dye retention is improved and consequently dye use is reduced, energy is saved in the curing step, productivity and dimensional stability of the fibrous substrate are improved, yellowing caused by heat is reduced, and, when the curing is in gas-fired ovens, exposure to nitrogen oxide (NO<sub>x</sub>) and the resultant discoloration is reduced.

When applied to Class A Substrates, including textiles and fabrics, a low temperature cure at ambient temperature about to 160°C is used to set the coating on the fibers and develop the desired repellency properties. The preferred cure temperature is from about 80° to about 130°C. While repellency is achieved without an elevated temperature cure, curing at the preferred temperature enhances repellency. The conventional high temperature cure of about 165°C is avoided.

The amount of polymer dispersion applied to the Class A Substrate surface is an amount sufficient to provide at least 200 and preferably 800 - 5,000 parts per million by weight (microgram/g) of fluorine based on the weight of the dry fibrous substrate. Higher loadings increase cost without significant improvements in repellency.

While application as an aqueous dispersion is preferred for reasons of cost, application hazards, and environmental impact, application can also be made from solution or dispersion in solvents.

The polymer dispersion is applied to Class A Substrates, including, but not limited to, woven and non-woven fabrics made from natural and synthetic fibers, including polyamides and aramids, polyesters, polyolefins, cotton, wool, silk, rayon, and mixtures of such fiber compositions, by conventional methods such as

padding, spraying, foam, and dipping. The polymer dispersions can also be co-applied simultaneously or sequentially with stainblockers, softeners, wetting agents, antistats, and permanent press aids.

5           The polymers of the current invention are, also useful for treating Class B Substrates wherein the oil and water repellent properties of the coated substrate develop after drying at ambient or under mild forced air conditions. A particular example, natural leather, illustrates the advantages. Polymers of the present invention are applied by spray onto dry or semi-wet hides or are applied during  
10   the wet processing, or after completion of the normal tanning, retanning or dyeing process. Preferably the polymer is applied while the natural leather is in a swollen state. In contrast to the prior art, the treated natural leather does not require a heat cure or lengthy storage time before the repellency properties are fully developed. This advantage enables fabrication of the natural leather article immediately after  
15   natural leather drying and processing and eliminates the storage facilities and delay currently needed for development of the functional natural leather properties. Additionally, the ability to add the dispersion during the wet treatment stage of the natural leather preparation permits the treatment to be effective throughout the natural leather thickness, as opposed to surface treatments of the  
20   finished natural leather. Thus water- and oil- repellency is retained when the natural leather is cut during fabrication, or when the natural leather surface is damaged or abraded in use.

          The amount of polymer dispersion applied to the natural leather is an  
25   amount to provide a dry natural leather containing at least 0.2, and preferably 0.4 to about 20 g of fluorine/m<sup>2</sup>. Higher loadings increase cost without significant improvements in repellency. The fluorine content of the polymer is known by calculation based on the synthesis, or by analysis of the polymer. Application levels for other Class B Substrates are the same.

30

          Alternatively, the polymer dispersions of this invention are applied topically to Class A and Class B Substrates, including carpets, curtains, upholstery fabrics, clothing, wood, masonry, and dry or semi-wet natural leather by conventional methods such as spraying, padding, or swabbing, and the like.

Class C Substrates comprise synthetic suede leathers. For application to synthetic suede leathers, the emulsification of the reaction mass is omitted, resulting in a dispersion with average particle size 250 – 2000 nm and preferably 5 300 – 700 nm. Unexpectedly, the products of this invention provide enhanced performance at this larger particle size. When the dispersion particle size is reduced to the more conventional range of 130 – 150 nm, the color fastness and laundry air dry properties are significantly inferior for applications to synthetic suede leather. While not wishing to be bound by theory, we believe that the larger 10 particles are deposited near the very porous synthetic suede leather surface. Synthetic suede leather is much more porous than natural leather. Application using smaller particles, while effective on Class A and B substrates, loses effectiveness if the penetration into the synthetic suede leather is too deep. The preferred range of 380 – 700 nm balances this penetration effect with the 15 progressively decreasing dispersion stability occurring as the dispersion size is further increased. Beyond 2000 nm, dispersions are impracticably unstable.

Benefits from the application of the larger particle sized polymers of this invention to synthetic suede leather include durable oil and water repellency and 20 the ability of the treated synthetic suede leather to recover or retain the oil and water repellency after laundering and air drying without a heating step. The laundry air dry performance of synthetic suede leather is measured by standard test methods described below. The desired dynamic water repellency rating (Test Method 3) using the water spray test for synthetic suede leather after 5 wash and 25 air-dry cycles is at least 70, preferably 80. The desired oil repellency rating (Test Method 1) for synthetic suede leather after five wash and air-dry cycles is at least 2, preferably 3.

Additionally, the treated synthetic suede leather demonstrates improved 30 color fastness after abrasion, as measure by a standard test method for color migration. The desired color fastness rating (Test Method 6) for synthetic suede leather after 10 abrasion cycles using cotton fabric is 3 or more.

For Class C substrates, pre-wash dynamic water repellency (Test Method 3) may be further improved by the addition of conventional bath additives for synthetic suede leathers.

5           The present invention further comprises a substrate treated to have durable oil and water repellency. The substrate is contacted with the polymer of the present invention as previously described. A high temperature cure is not required after application for development of the repellent properties. For Class A and Class C Substrates no heat treatment after laundering is needed to restore the  
10 repellent properties. Thus the present invention enhances the properties of the substrate.

Advantages of the present invention are further illustrated by the following examples. In Test Methods 1 and 2 the oil and water repellency rating give a  
15 measure of the theoretical ability of the surface treatment to prevent water and oil from wetting the substrate surface. The oil repellency rating corresponds to the most penetrating test oil (the highest numbered Test Oil) in Table 4 that does not penetrate, wick, or wet the substrate after 30 seconds contact. The water repellency rating corresponds to the most penetrating water/isopropanol mixture  
20 (the highest numbered Water Test Solution) in Table 5 that does not penetrate, wick, or wet the substrate after 10 seconds contact.

### TEST METHODS

25   Test Method 1. Oil Repellency (for Class A, B, and C Substrates).

The treated fabric samples were tested for oil repellency by a modification of the American Association of textile Chemists and Colorists (AATCC) standard Test Method No. 118, conducted as follows. A fabric sample, treated with an  
30 aqueous dispersion of polymer as previously described, is conditioned for a minimum of 2 hours at 23°C + 20% relative humidity and 65°C and 10% relative humidity. A series of organic liquids, identified below in Table 4, are then applied dropwise to the fabric samples. Beginning with the lowest numbered test liquid (Repellency Rating No. 1), one drop (approximately 5 mm in diameter or

0.05 mL volume) is placed on each of three locations at least 5 mm apart. The drops are observed for 30 seconds. If, at the end of this period, two of the three drops are still spherical in shape with no wicking around the drops, three drops of the next highest numbered liquid are placed on adjacent sites and similarly observed for 30 seconds. The procedure is continued until one of the test liquids results in two of the three drops failing to remain spherical to hemispherical, or wetting or wicking occurs.

The oil repellency rating of the fabric is the highest numbered test liquid for which two of the three drops remained spherical to hemispherical, with no wicking for 30 seconds. In general, treated fabrics with a rating of 3 or more are considered good to excellent; fabrics having a rating of one or greater can be used in certain applications.

Table 4. Oil Repellency Test Liquids

Oil Drop Rating (Test Oils)		
Test Oil #	Composition	Surface Tension Dynes/cm 25°C
1	NUJOL mineral oil	31.0
2	65:35 NUJOL:n-hexadecane*	29.2
3	n-hexadecane	27.3
4	n-tetradecane	26.2
5	n-dodecane	24.6
6	n-decane	23.6

NUJOL is a mineral oil available from Schering-Plough, Memphis TN.

\* Composition by volume at 21°C.

## Test Method 2. Water Repellency (for Class A and B Substrates).

The water repellency of a treated substrate determines the resistance of a treated substrate to wetting by aqueous liquids. Drops of water-alcohol mixtures of varying surface tensions are placed on the substrate and the extent of surface

- wetting is determined visually. The test provides a rough index of aqueous stain resistance. The higher the water repellency rating, the better the resistance of a finished substrate to staining by water-based substances. In general, treated substrates with a rating of 3 or more are considered good to excellent. The composition of standard test liquids is shown in the following Table 5.

Table 5: Water Repellency Test Liquids.

Water Drop Rating (Test Solutions.)		
Test Soln. #	Water/ Isopropanol (% Vol.)	Surface Tension Dynes/cm at 24°C
1	98/2	59.0
2	95/5	50.0
3	90/10	42.0
4	80/20	33.0
5	70/30	27.5
6	60/40	

- 10 Test Method 3. Measurement of Dynamic Water Repellency (for Class C Substrates).

Dynamic water repellency was measured according to the American Association of Textile Chemists and Colorists (AATCC) Method 22-1996.

- 15 Samples are visually scored by reference to published standards, with a rating of 100 denoting no water penetration or surface adhesion. A rating of 90 denotes slight random sticking or wetting, lower values indicate progressively greater wetting.

- 20 Test Method 4. Laundering and Air Dry Procedures (for Class A and C Substrates).

Laundering was performed with 19 g AATCC 1993 Standard Reference Detergent WOB in an automatic washer with washer controls set at high water

level, normal 12 minute wash cycle, and warm wash (40°C), cold rinse. For Class A Substrates only, polyester ballast was added to the fabric samples to give a total dry load of about 4 lb. Fabric samples were not dried between consecutive wash cycles. The samples were allowed to dry on a mesh screen at room temperature  
5 for 24 hours before rating.

Test Method 5. Particle Size Measurements (Class C Substrates).

Particle size was measured by the laser light scattering method using a  
10 Coulter Counter Model N4MD, manufactured by Langley Ford Instruments, Amherst MA.

Test Method 6. Color Fastness to Crocking (Class C Substrates).

15 Color fastness to crocking was measured by AATCC Test method 8-1996.

### MATERIALS

The following materials were used in the examples.

20

DESMODUR N-100 and DESMODUR N-3300 contain hexamethylene diisocyanate homopolymers. DESMODUR N-100 is a hexamethylene diisocyanate-based polymeric isocyanate containing biuret groups, and DESMODUR N-3300 is a hexamethylene diisocyanate-based biuret-containing  
25 polymeric isocyanate with the hexamethylene diisocyanate converted to an isocyanurate ring. Both are available from Bayer Corporation, Pittsburgh PA.

ISO FOL 18T is a mixture of branched chain alcohols comprising 2-hexyl- and 2-octyl-decanol, and 2-hexyl- and 2-octyl-dodecanol, available from  
30 CONDEA-Vista Co., Houston TX.

LODYNE 941 is a fluorinated diol of the structure  
 $(\text{HOCH}_2)_2\text{C}(\text{CH}_2\text{SCH}_2\text{CH}_2\text{R}_f)_2$  and LODYNE 921B is a thiol of the structure



$F(CF_2CF_2)_nCH_2CH_2SH$  ( $n = 2-5$ ). Both are available from Ciba Specialty Chemicals, High Point, NC

5 NUJOL is a mineral oil available from Schering-Plough, Inc.,  
Memphis TN.

ZONYL BA and ZONYL BA-N are mixed 1,1,2,2-tetrahydroperfluoro-1-  
alkanols, predominately  $C_8$ ,  $C_{10}$ ,  $C_{12}$ , and  $C_{14}$  with small amounts of  $C_6$ ,  $C_{16}$ ,  
and  $C_{18}$ , available from E. I. du Pont de Nemours and Company, Wilmington DE.  
10

ZONYL FMX and ZONYL 8300 are commercially available repellent  
products available from E. I. du Pont de Nemours and Co. Wilmington DE.

MIBK indicates methylisobutylketone.  
15

The synthetic suede leather used in the examples was a commercially  
available polyurethane-based leather designated K-7600-751 and available from  
Kuraray (Osaka, Japan).

## 20 EXAMPLES

### Example 1.

25 Stearyl alcohol (101.3 g, 0.37 mol), ISOFOL 18T (101.3 g, 0.37 mol),  
dimethylethanolamine (7.0 g, 0.08 mol), DESMODUR N-100 (60% solution in  
MIBK, 600.0 g), and melted ZONYL BA (367.0 g, 0.77 mol) were added to a  
2000-mL round bottom flask fitted with a condenser, thermocouple, and agitator.  
The solution was heated to 60-65°C and 15-30 g dibutyltin dilaurate solution (0.4  
wt% in MIBK) added. The temperature increased exothermically from 67 to  
30 103°C upon addition of catalyst solution. After the exotherm, the temperature  
was set to 90°C and the solution heated with stirring at 90°C for 14 hours. The  
temperature was lowered to 75°C and 40.0 g water plus 300.0 g MIBK were  
added. The reaction solution was heated at 75°C with stirring for 3 hours.

## Example 2.

Stearyl alcohol (51.5 g, 0.19 mol), ISOFOL 18T (52.4 g, 0.19 mol),  
5 dimethylethanolamine (1.8 g, 0.02 mol), DESMODUR N-100 (60% solution in  
MIBK, 300.0 g), MIBK (130.0 g), and melted ZONYL BA (190.0 g, 0.40 mol)  
were added to a 1000-mL round bottom flask fitted with a condenser,  
thermocouple, and agitator. The solution was heated to 50 - 60°C and 15 g  
dibutyltin dilaurate solution (0.4 wt% in MIBK) added. The temperature  
10 increased exothermically from 55 to 74°C upon addition of catalyst solution.  
After the exotherm, the temperature was set to 90°C and the solution heated with  
stirring at 90°C for 14 hours. The temperature was lowered to 75°C and 50.0 g  
water plus 70.0 g MIBK were added. The reaction solution was heated at 75°C  
with stirring for 3 hours.

15

## Example 3.

Stearyl alcohol (67.8 g, 0.25 mol), ISOFOL 18T (41.4 g, 0.15 mol),  
DESMODUR N-100 (60% solution in MIBK, 300.0 g), MIBK (100.0 g), and  
20 melted ZONYL BA (189.6 g, 0.40 mol) were added to a 1000-mL round bottom  
flask fitted with a condenser, thermocouple, and agitator. The solution was heated  
to 60 - 65°C and 15 g dibutyltin dilaurate solution (0.4 wt% in MIBK) added.  
The temperature increased exothermically from 60 to 88°C upon addition of  
catalyst solution. After the exotherm, the temperature was set to 90°C and the  
25 solution heated with stirring at 90°C for 14 hours. The temperature was lowered  
to 75°C and 50.0 g water plus 90.0 g MIBK were added. The reaction solution  
was heated at 75°C with stirring for 3 hours.

30

## Example 4.

DESMODUR N-100 (60% solution in MIBK, 300.0 g), MIBK (100.0 g),  
and melted ZONYL BA (380.0 g, 0.80 mol) were added to a 1000-mL round  
bottom flask fitted with a condenser, thermocouple, and agitator. The solution

was heated to 55 - 60°C and 15 g dibutyltin dilaurate solution (0.4 wt% in MIBK) added. The temperature increased exothermically from 54 to 85°C upon addition of catalyst solution. After the exotherm, the temperature was set to 90°C and the solution heated with stirring at 90°C for 14 hours. The temperature was lowered  
5 to 75°C and 50.0 g water plus 100.0 g MIBK were added. The reaction solution was heated at 75°C with stirring for 3 hours.

Example 5.

10 Stearyl alcohol (27.1 g, 0.10 mol), ISO FOL 18T (27.6 g, 0.10 mol), DESMODUR N-100 (60% solution in MIBK, 300.0 g), MIBK (100.0 g), and melted ZONYL BA (285.0 g, 0.60 mol) were added to a 1000-mL round bottom flask fitted with a condenser, thermocouple, and agitator. The solution was heated to 55 - 60°C and 15 g dibutyltin dilaurate solution (0.4 wt% in MIBK) added.  
15 The temperature increased exothermically from 56 to 78°C upon addition of catalyst solution. After the exotherm, the temperature was set to 90°C and the solution heated with stirring at 90°C for 14 hours. The temperature was lowered to 75°C and 50.0 g water plus 80.0 g MIBK were added. The reaction solution was heated at 75°C with stirring for 3 hours.

20

Example 6.

Stearyl alcohol (46.1 g, 0.17 mol), ISO FOL 18T (46.9 g, 0.17 mol), DESMODUR N-100 (60% solution in MIBK, 300.0 g), MIBK (100.0 g), and  
25 melted ZONYL BA (175.8 g, 0.37 mol) were added to a 1000-mL round bottom flask fitted with a condenser, thermocouple, and agitator. The solution was heated to 55 - 60°C and 15 g dibutyltin dilaurate solution (0.4 wt% in MIBK) added. The temperature increased exothermically from 55 to 84°C upon addition of catalyst solution. After the exotherm, the temperature was set to 90°C and the  
30 solution heated with stirring at 90°C for 14 hours. The temperature was lowered to 75°C and 50.0 g water plus 100.0 g MIBK were added. The reaction solution was heated at 75°C with stirring for 3 hours.

## Example 7.

Stearyl alcohol (40.7 g, 0.15 mol), ISOFOL 18T (69.0 g, 0.25 mol),  
5 DESMODUR N-100 (60% solution in MIBK, 300.0 g), MIBK (100.0 g), and  
melted ZONYL BA (189.6 g, 0.40 mol) were added to a 1000-mL round bottom  
flask fitted with a condenser, thermocouple, and agitator. The solution was heated  
to 55 - 60°C and 15 g dibutyltin dilaurate solution (0.4 wt% in MIBK) added.  
The temperature increased exothermically from 57 to 86°C upon addition of  
10 catalyst solution. After the exotherm, the temperature was set to 90°C and the  
solution heated with stirring at 90°C for 14 hours. The temperature was lowered  
to 75°C and 50.0 g water plus 100.0 g MIBK were added. The reaction solution  
was heated at 75°C with stirring for 3 hours.

## 15 Example 8.

Stearyl alcohol (108.4 g, 0.40 mol), ISOFOL 18T (108.6 g, 0.39 mol),  
DESMODUR N-100 (60% solution in MIBK, 600.0 g), and melted ZONYL BA  
(379.2 g, 0.80 mol) were added to a 2000-mL round bottom flask fitted with a  
20 condenser, thermocouple, and agitator. The solution was heated to 55-60°C and  
15-30 g dibutyltin dilaurate solution (0.4 wt% in MIBK) added. The temperature  
increased exothermically from 60 to 100°C upon addition of catalyst solution.  
After the exotherm, the temperature was set to 90°C and the solution heated with  
stirring at 90°C for 14 hours. The temperature was lowered to 75°C and 40.0 g  
25 water plus 300.0 g MIBK were added. The reaction solution was heated at 75°C  
with stirring for 3 hours.

## Example 9.

30 Stearyl alcohol (81.3 g, 0.30 mol), ISOFOL 18T (82.8 g, 0.30 mol),  
DESMODUR N-100 (60% solution in MIBK, 300.0 g), MIBK (100.0 g), and  
melted ZONYL BA (95.0 g, 0.20 mol) were added to a 1000-mL round bottom  
flask fitted with a condenser, thermocouple, and agitator. The solution was heated

to 55 - 60°C and 15 g dibutyltin dilaurate solution (0.4 wt% in MIBK) added.

The temperature increased exothermically from 55 to 87°C upon addition of catalyst solution. After the exotherm, the temperature was set to 90°C and the solution heated with stirring at 90°C for 14 hours. The temperature was lowered to 75°C and 50.0 g water plus 100.0 g MIBK were added. The reaction solution was heated at 75°C with stirring for 3 hours.

#### Example 10.

ISOFOL 18T (109.7 g, 0.40 mol), DESMODUR N-100 (60% solution in MIBK, 300.0 g), and melted ZONYL BA (189.6 g, 0.40 mol) were added to a 1000-mL round bottom flask fitted with a condenser, thermocouple, and agitator. The solution was heated to 55 - 60°C and 15 g dibutyltin dilaurate solution (0.4 wt% in MIBK) added. The temperature increased exothermically from 59 to 82°C upon addition of catalyst solution. After the exotherm, the temperature was set to 90°C and the solution heated with stirring at 90°C for 14 hours. The temperature was lowered to 75°C and 20.0 g water plus 150.0 g MIBK were added. The reaction solution was heated at 75°C with stirring for 3 hours.

#### Example 11.

Stearyl alcohol (67.8 g, 0.25 mol), ISOFOL 18T (69.0 g, 0.25 mol), DESMODUR N-100 (60% solution in MIBK, 300.0 g), MIBK (100.0 g), and melted ZONYL BA (217.1 g, 0.45 mol) were added to a 1000-mL round bottom flask fitted with a condenser, thermocouple, and agitator. The solution was heated to 60 - 65°C and 15 g dibutyltin dilaurate solution (0.4 wt% in MIBK) added. The temperature increased exothermically from 68 to 85°C upon addition of catalyst solution. After the exotherm, the temperature was set to 90°C and the solution heated with stirring at 90°C for 14 hours. The temperature was lowered to 75°C and 50.0 g water plus 100.0 g MIBK were added. The reaction solution was heated at 75°C with stirring for 3 hours.

#### Example 12.

Stearyl alcohol (107.5 g, 0.40 mol), DESMODUR N-100 (60% solution in MIBK, 300.0 g), and melted ZONYL BA (189.6 g, 0.40 mol) were added to a 1000-mL round bottom flask fitted with a condenser, thermocouple, and agitator.

- 5 The solution was heated to 60 - 65°C and 15 g dibutyltin dilaurate solution (0.4 wt% in MIBK) added. The temperature increased exothermically from 60 to 88°C upon addition of catalyst solution. After the exotherm, the temperature was set to 90°C and the solution heated with stirring at 90°C for 14 hours. The temperature was lowered to 75°C and 20.0 g water plus 150.0 g MIBK were
- 10 added. The reaction solution was heated at 75°C with stirring for 3 hours.

The ratios of reactants shown in Table 6 are listed on a molar basis per 100 isocyanate groups.

15 Table 6: Reactants on Molar Basis

Example	Fluoroalcohol (Reactant 2)	Alcohol (Reactant 3)			Amine (Reactant 3)
		Total	Straight Chain	Branched Chain	
2	40	38	19	19	0.002
3	40	40	25	15	0
4	80	0	0	0	0
5	60	20	10	10	0
6	37	34	17	17	0
7	40	40	15	25	0
8	40	40	20	20	0
9	20	60	30	30	0
10	40	40	0	40	0
11	45	50	25	25	0
12	40	40	40	0	0

Example 13.

Water at 75°C (400 g), cationic surfactant ARMEEN DM-18 (4.0 g), and acetic acid (0.24 g) were combined in a 1000-mL round bottom flask. A fluoroethane polymer prepared as in Examples 1-11 (252.8 g) was heated to 60°C and added to the flask containing the water/surfactant mixture. The solution was emulsified using a microfluidizer and distilled under vacuum to remove the MIBK. The resulting solution was 30.5% solids.

A solution was made by mixing 5 g of the fluorourethane dispersion of Example 12 in 95 g of a 10% aqueous solution of isopropanol. The solution was applied to the surface of various substrates as indicated in Table 7 and dried for two days at ambient temperature. Repellency performance was evaluated according to Test Method 1 and Test Method 2 described above and the resulting data are shown in Table 7.

Table 7a: Ambient Cure Test Results for Class A Substrates (Oil: Test Method 1, Water: Test Method 2)

Example	100% PES*		100% Nylon		65/35 PES/Co*		100% Silk		100% Cotton		Wool	
	Oil	Water	Oil	Water	Oil	Water	Oil	Water	Oil	Water	Oil	Water
Control (no treatment)	0	0	0	3	0	0	0	0	0	0	0	3
13	5	5	3	5	5	5	4	4	5	5	2	4

\* PES = Polyester, 65/35 PES/Co = 65% polyester/ 35% cotton

Table 7b: Ambient Cure Test Results for Class B Substrates (Test Methods as in Table 6a)

	Stone		Wood		Paper		Natural Leather	
Example	Oil	Water	Oil	Water	Oil	Water	Oil	Water
Control (no treatment)	0	0	0	0	0	0	0	0
13	1	3	5	4	6	5	5	4

The performance data in Table 7 showed that the fluorourethane polymers imparted repellency to Class A and Class B substrates without an elevated temperature cure.

#### Example 14.

Water at 75°C (300 g), fluorourethane polymer prepared as in Example 1 (100.0 g), and acetic acid (20.0 g) were combined in a flask. The solution was emulsified using a microfluidizer, and distilled under vacuum to remove the MIBK.

#### Example 15.

Dispersions of Examples 1, 8, 10 and 12 were prepared as in Example 13. The comparative examples were existing commercially available oil and water repellent products. OLEOPHOBOL C was from Ciba Specialty Chemicals, Langweid, Germany; ZONYL FMX and ZONYL 8300 were from E. I. du Pont de Nemours and Company, Wilmington, DE; and AG710 was from Asahi Products, Japan. Examples 1, 8, 10, 12 and 14 and the comparative examples as listed in Table 8 were pad applied at equal fluorine loading on 100% polyester fleece fabric. The fabrics were cured at 120°C for 15 minutes immediately after padding. The fabrics were air-dried overnight at room temperature after laundering, before rating. The oil repellency and water repellency performance of



the treated fabrics were evaluated according to Test Methods 1 and 2 initially and after 5 and 10 home launderings.

Table 8: Laundry Air Dry Repellency Performance

	Oil Repellency (Test Method 1)			Water Repellency (Test Method 2)		
	Initial	5 HWAD*	10 HWAD	Initial	5 HWAD	10 HWAD
<b>Example</b>						
<b>1</b>	5	5	2	5	5	5
<b>8</b>	5	5	3	5	6	6
<b>10</b>	6	5	2	6	5	5
<b>12</b>	6	0	0	6	4	3
<b>14</b>	3	5		3	5	
<b>Comparative Examples</b>						
<b>OLEO-PHOBOL C</b>	5	0	0	6	3	3
<b>ZONYL FMX</b>	3	0	0	5	3	4
<b>ZONYL 8300</b>	3	0	0	6	3	3
<b>Asahi AG710</b>	4	0	0	6	3	3

\* 5 or 10 HWAD = 5 or 10 home wash and ambient temperature air dry cycles

The data for Examples 1, 8, 10, 12, and 13 demonstrate that use of a low temperature cure is sufficient for imparting oil repellency and water repellency to treated substrates, and that use of a high temperature cure is not required. In examples 8, 10 and Comparative Example A the straight chain mole %/branched chain mole % ratio for the fluoroalcohol (Reactant 2) employed was 50/50, 0/100, and 100/0, respectively. This data showed that superior retention of repellency when air drying without heat after laundering was obtained when some branched chain Reactant 2 was employed. The data from examples 1 and 8 showed that durable performance was achieved from either a nonionic polymer or cationic polymer. Existing commercial repellent products did not provide durable laundry

air-dry performance. Data from Examples 1 and 14 showed that low temperature cure and laundry air dry performance was achieved from a self-dispersed cationic polymer or a cationic polymer dispersed with surfactants.

5 Example 16.

ZONYL BA (90 g), 12 g of stearyl alcohol, 12 g of ISOFOL 18T, 100 g of DESMODUR N-100 (60% solution in MIBK) were added to a 500-ml round bottom flask fitted with a condenser, thermometer, and agitator. The solution was  
10 heated to 50°C and 2 drops of dibutyltin dilaurate was added. The temperature increased exothermically from 51°C to 95°C. After the exotherm, the temperature was set to 90°C and the solution heated with stirring at 90°C for 3 hours. Then 10 g of N,N-dimethylethanolamine was added with 2 drops of dibutyltin dilaurate. After the exotherm, the temperature was set to 90°C and the solution heated with  
15 stirring at 90°C for another 2 hours. The temperature was lowered to 63°C, and 1.6 g of water and 106.4 g of MIBK were added. The reaction solution was heated at 75°C with stirring for 3 hours. The temperature was lowered to 60°C, 602 g of water (at 60°C) and 9.3 g of acetic acid were added. 150 g of this material was transferred to a laboratory blender and then agitated for 6 min.  
20 MIBK was removed under vacuum distillation. The particle size of dispersed material was 289 nm.

Example 17.

25 ZONYL BA (90 g), 12 g of stearyl alcohol, 12 g of ISOFOL 18T, 100 g of DESMODUR N-100 (60% solution in MIBK) were added to a 500-ml round bottom flask fitted with a condenser, thermometer, and agitator. The solution was heated to 50°C and 2 drops of dibutyltin dilaurate was added. The temperature increased exothermically from 51°C to 95°C. After the exotherm, the temperature  
30 was set to 90°C and the solution heated with stirring at 90°C for 3 hours. Then 10 g of N,N-dimethylethanolamine were added with 2 drops of dibutyltin dilaurate. After the exotherm, the temperature was set to 90°C and the solution heated with stirring at 90°C for another 2 hours. The temperature was lowered to 63°C and 660 g of water (at 60°C) and 14 g of acetic acid were added. The reaction solution

was heated at 75°C with stirring for 3 hours. MIBK was removed under vacuum distillation. The particle size of dispersed material was 597 nm.

Example 18.

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ZONYL BA (77 g), 12 g of stearyl alcohol, 8 g of ISOFOL 18T, 100 g of DESMODUR N-100 (60% solution in MIBK) were added to a 500-ml round bottom flask fitted with a condenser, thermometer, and agitator. The solution was heated to 50°C, 2 drops of dibutyltin dilaurate was added. The temperature increased exothermically from 51°C to 95°C. After the exotherm, the temperature was set to 90°C and the solution heated with stirring at 90°C for 3 hours. Then 7 g of N,N-dimethylethanolamine was added with 2 drops of dibutyltin dilaurate. After the exotherm, the temperature was set to 90°C and the solution heated with stirring at 90°C for another 2 hours. The temperature was lowered to 63°C and 660 g of water (at 60°C) and 8 g of acetic acid were added. The reaction solution was heated at 75°C with stirring for 3 hours. MIBK was removed under vacuum distillation. The particle size of dispersed material was 333 nm.

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Example 19.

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ZONYL BA (90 g), 12 g of stearyl alcohol, 7 g of ISOFOL 18T, 100 g of DESMODUR N-100 (60% solution in MIBK) were added to a 500-ml round bottom flask fitted with a condenser, thermometer, and agitator. The solution was heated to 50°C and 2 drops of dibutyltin dilaurate was added. The temperature increased exothermically from 51°C to 95°C. After the exotherm, the temperature was set to 90°C and the solution heated with stirring at 90°C for 3 hours. Then 12.5 g of N,N-dimethylethanolamine was added with 2 drops of dibutyltin dilaurate. After the exotherm, the temperature was set to 90°C and the solution heated with stirring at 90°C for another 2 hours. The temperature was lowered to 63°C, and 1.6 g of water and 106.4 g of MIBK were added. The reaction solution was heated at 75°C with stirring for 3 hours. The temperature was lowered to 60°C, 653 g of water (at 60°C) and 9.5 g of acetic acid were added. 150 g of this material was transferred to a laboratory blender and then

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agitated for 2 min. MIBK was removed under vacuum distillation. The particle size of dispersed material was 277 nm.

#### Example 20.

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Example 20 describes the preparation and use of the padding bath. A bath was prepared containing 24 g fluoroacrylate copolymer prepared as described in US Patent 4,742,140; 9.6 g of fluorocarbamate prepared as in Examples 16, 17, 18, 19, and Comparative Examples A; 1.6 g of ethylene glycol; 6.6 g isopropyl  
10 alcohol; 0.6 g AEROTEX 3730 (from Goodrich Co., Charlotte, NC); 0.034 g of ammonium chloride; and 159.17 g water. The padding conditions were 2 dips and about 55% by weight pickup, and a curing condition of 140°C for 2.5 min. The synthetic suede leather was K-7600-751 from Kuraray. The results are shown in Table 9.

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#### Comparative Example A.

90 g of ZONYL BA, 12 g of stearyl alcohol, 12 g of ISOFOL 18T, 100 g of DESMODUR N-100 (60% solution in MIBK) were added to a 500-ml round  
20 bottom flask fitted with a condenser, thermometer, and agitator. The solution was heated to 50°C and 2 drops of dibutyltin dilaurate was added. The temperature increased exothermically from 51°C to 95°C. After the exotherm, the temperature was set to 90°C and the solution heated with stirring at 90°C for 3 hours. Then 10 g of N,N-dimethylethanolamine was added with 2 drops of dibutyltin dilaurate.  
25 After the exotherm, the temperature was set to 90°C and the solution heated with stirring at 90°C for another 2 hours. The temperature was lowered to 63°C, and 1.6 g of water and 106.4 g of MIBK was added. The reaction solution was heated at 75°C with stirring for 3 hours. The temperature was lowered to 60°C, 602 g of water (at 60°C) and 4.8 g of acetic acid were added, and then the mixture was  
30 emulsified using a microfluidizer. MIBK was removed under vacuum distillation. The particle size of emulsified material was 110 nm. The padding bath was as described in Example 20, containing fluoroacrylate polymer.

#### Comparative Example B.

Untreated synthetic suede leather (Kuraray K-7600-751) was used as a control.

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Table 9. Formulation Detail and Test Results on Synthetic Suede Leather.

Example #	Particle Size (nm) (Test Method 5)	Color Fastness (Test Method 6)	Laundry air dry spray (Test Method 3) Initial/After 5 Cycles*	Laundry air dry oil (Test Method 1) Initial/After 5 Cycles*
<b>Examples</b>				
16	289	3	90+ / 70+	5 / 2
17	597	3	90+ / 80	7 / 2+
18	333	3	90 / 80	5 / 3
19a*	277	3	100 / 80	5 / 3
19b*	277	3	70 / 80	4 / 3
<b>Comparative Examples</b>				
A	110	1	80+ / 70-	5 / 0
B	--	3	70- / 50	0 / 0
<b>Monomer Weights for the Above Fluorocarbamates</b> (Monomer molar ratio to isocyanate group of DESMODUR N-100)				
<b>Example:</b>		<b>16, 17, A</b>	<b>18</b>	<b>19</b>
DESMODUR N-100		100 (N/A)	100 (N/A)	100 (N/A)
ZONYL BA		90 (58.35)	77 (49.92)	90 (58.35)
Stearyl alcohol		12 (14.07)	12 (14.07)	12 (14.07)
ISO FOL 18T		12 (14.07)	8 (9.38)	7 (8.21)
N,N-dimethylethanolamine		10 (34.48)	7 (24.14)	12.5 (26.77)
Remaining isocyanate group		(0)	(2.49)	(0)

\* The padding bath for example 19a contained fluoroacrylate copolymer as described in Example 20. Example 19b uses the same fluorocarbamate as

Example 19a, but the padding bath did not contain the fluoroacrylate polymer.

The same fluorine level in the bath was maintained by increasing the amount of fluorocarbamate. The effect of the fluoroacrylate bath additive is to further enhance the pre-wash water spray rating, while having no discernible effect for  
5 post wash performance.

Table 9 shows the Examples 16 – 19 provide the required combination of color fastness, water spray rating, and oil repellency desired for synthetic suede leather.

The untreated control (Comparative Example C) and Comparative Examples A  
10 and B (with particle sizes less than 250 nm) fail two or three of these criteria.

**WHAT IS CLAIMED IS :**

1. A polymer having at least one urea linkage derived by contacting
  - (1) at least one polyisocyanate, or mixture of polyisocyanates, (2) at least one fluorocarbon alcohol, fluorocarbon thiol or fluorocarbon amine, (3) at least one fluorocarbon alcohol, fluorocarbon thiol or fluorocarbon amine, (3) at least one alcohol, amine or thiol, and then (4) at least one linking agent.
2. The polymer of Claim 1 dispersed in water with an emulsifying agent or surfactant.
3. The polymer of Claim 1 wherein the polyisocyanate contains at least three isocyanate groups or is a diisocyanate precursor of a polyisocyanate containing at least three isocyanate groups.
4. The polymer of Claim 1 wherein the fluorocarbon alcohol, fluorocarbon thiol or fluorocarbon amine is of formula
 
$$R_f-X-Y-H$$
 wherein
  - $R_f$  is a  $C_4$ - $C_{20}$  linear or branched fluorocarbon chain,
  - $X$  is a divalent linking radical of formula  $-(CH_2)_n-$  or  $-SO_2N(R_1)-CH_2CH_2-$  wherein  $n$  is 1 to about 20, and  $R_1$  is an alkyl of 1 to about 4 carbon atoms, and
  - $Y$  is  $-O-$ ,  $-S-$  or  $-N(R_1)_2-$ .
5. The polymer of Claim 5 wherein  $R_f-X-$  is  $F(CF_2)_q(CH_2)_n-$  wherein  $n$  is 1 to about 20 and  $q$  is from about 4 to about 20.
6. The polymer of Claim 1 wherein the alcohol, amine or thiol is a formula selected from the group consisting of  $H(CH_2)_x-OH$ ,  $H(CH_2)_x-NH_2$ ,  $H(CH_2)_x-SH$ ,  $C_yH_{(2y+1)}CH_2OH$ ,  $C_yH_{(2y+1)}CH_2NH_2$ ,  $C_yH_{(2y+1)}CH_2SH$ , and a mixture thereof, wherein  $x$  is from about 12 to about 20 and  $y$  is from about 15

to about 19, and wherein the alcohol, amine, or thiol has a molar ratio of branched chain to straight chain of from about 1:0 to about 1:1.

7. The polymer of Claim 1 wherein the alcohol, amine, or thiol  
5 contains at least one group capable of reacting with an isocyanate and at least one quaternizable group.

8. The polymer of Claim 1 wherein the linking agent is a compound  
10 containing a hydroxy group.

9. The polymer of Claim 1 derived by contacting (1) at least one  
polyisocyanate, or mixture of polyisocyanates, (2) at least one fluorocarbon  
alcohol, fluorocarbon thiol or fluorocarbon amine, (3) at least one alcohol, amine  
or thiol, and then (4) at least one chemical species containing at least one group  
15 capable of reacting with an isocyanate and at least one quaternizable group, and  
then (5) at least one linking agent.

10. The polymer of Claim 1 wherein the molar ratio of reactants per  
100 isocyanate groups is from about 31 to about 60 for the fluorocarbon alcohol,  
20 fluorocarbon thiol, or fluorocarbon amine, from about 31 to about 65 for the  
alcohol, amine or thiol, and from about 0 to about 30 for the linking agent.

11. A method of imparting oil repellency and water repellency to a  
fibrous substrate or a wood, masonry or natural leather substrate comprising  
25 contacting said substrate with

A) a polymer having at least one urea linkage derived by contacting (1) at  
least one polyisocyanate, or mixture of polyisocyanates, (2) at least one  
fluorocarbon alcohol, fluorocarbon thiol, or fluorocarbon amine, (3) at least one  
alcohol, amine or thiol, and then (4) at least one linking agent, or  
30 B) a polymer is derived by contacting (1) at least one polyisocyanate, or  
mixture of polyisocyanates, (2) at least one fluorocarbon alcohol, fluorocarbon  
thiol or fluorocarbon amine, (3) at least one alcohol, amine or thiol, and then (4) at  
least one chemical species containing at least one group capable of reacting with



an isocyanate and at least one quaternizable group, and then (5) at least one linking agent,  
and wherein no curing step is employed after contacting the substrate with the polymer.

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12. The method of Claim 11 wherein the amount of polymer contacted with a fibrous substrate is sufficient to provide a fluorine content of at least about 200 microgram/g by weight of the fibrous substrate when dry, and the amount of polymer contacted with the wood, masonry or natural leather substrate is sufficient to provide a fluorine content of from about 0.2 to about 20 g fluorine/m<sup>2</sup>.

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13. A method of imparting oil repellency and water repellency to a synthetic suede leather substrate comprising contacting said substrate with

15 A) a polymer having at least one urea linkage derived by reacting (1) at least one polyisocyanate, or mixture of polyisocyanates, (2) at least one fluorocarbon alcohol, fluorocarbon thiol, or fluorocarbon amine, (3) at least one alcohol, amine or thiol, and then (4) optionally at least one linking agent, wherein the polymer has a particle size of a minimum of about 250 nm, or

20 B) a polymer prepared by contacting (1) at least one polyisocyanate, or mixture of polyisocyanates, (2) at least one fluorocarbon alcohol, fluorocarbon thiol or fluorocarbon amine, (3) at least one alcohol, amine or thiol, and then (4) at least one chemical species containing at least one group capable of reacting with an isocyanate and at least one quaternizable group, and then (5) optionally at least one linking agent, wherein the polymer has a particle size of a minimum of 250 nm.

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14. The method of Claim 13 wherein the amount of polymer contacted with the synthetic suede leather substrate is sufficient to provide a fluorine content of at least 0.6% by weight of the substrate.

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15. A fibrous substrate and a wood, masonry or natural leather substrate treated to have oil repellency and water repellency by the method of

Claim 11, and wherein the oil and water repellency is retained after laundering  
and air drying without use of a heat treatment.

16. A synthetic suede leather substrate treated to provide oil repellency  
5 and water repellency by the method of Claim 13.

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 00/21718

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 C08G18/28 D06M15/576 C14C11/00

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C08G D06M C14C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal, PAJ

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 692 566 A (ASAHI GLASS) 17 January 1996 (1996-01-17) page 2, line 34 -page 4, line 38; claims 1-3,6,7; examples PREPARATION,1,4	1-5
X	WO 96 12059 A (E.I. DU PONT DE NEMOURS) 25 April 1996 (1996-04-25) page 3, line 13 -page 7, line 36; claims 1-4; example 1	1-4
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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# INTERNATIONAL SEARCH REPORT

International Application No  
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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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